Not entered

PATENT COOPERATION TREATY

PCT

INTERNATIONAL PRELIMINARY EXAMINATION REPORT

(PCT Article 36 and Rule 70)

Applicant's or agent's file reference MOL0672-PCT	**FOR FURTHER ACTION**	See Notification of Transmittal of International Preliminary Examination Report (Form PCT/IPEA/416)
International application No. PCT/IB 03/04649	International filing date *(day/month/year)* 17.10.2003	Priority date *(day/month/year)* 18.10.2002
International Patent Classification (IPC) or both national classification and IPC C25C3/18		
Applicant MOLTECH INVENT S.A. et al.		

1. This international preliminary examination report has been prepared by this International Preliminary Examining Authority and is transmitted to the applicant according to Article 36.

2. This REPORT consists of a total of 4 sheets, including this cover sheet.

   ☒ This report is also accompanied by ANNEXES, i.e. sheets of the description, claims and/or drawings which have been amended and are the basis for this report and/or sheets containing rectifications made before this Authority (see Rule 70.16 and Section 607 of the Administrative Instructions under the PCT).

   These annexes consist of a total of 2 sheets.

3. This report contains indications relating to the following items:

   - I ☒ Basis of the opinion
   - II ☐ Priority
   - III ☐ Non-establishment of opinion with regard to novelty, inventive step and industrial applicability
   - IV ☐ Lack of unity of invention
   - V ☒ Reasoned statement under Rule 66.2(a)(ii) with regard to novelty, inventive step or industrial applicability; citations and explanations supporting such statement
   - VI ☐ Certain documents cited
   - VII ☐ Certain defects in the international application
   - VIII ☐ Certain observations on the international application

Date of submission of the demand	Date of completion of this report
12.05.2004	21.10.2004
Name and mailing address of the international preliminary examining authority: European Patent Office D-80298 Munich Tel. +49 89 2399 - 0 Tx: 523656 epmu d Fax: +49 89 2399 - 4465	Authorized Officer Mizera, E Telephone No. +49 89 2399-8580

INTERNATIONAL PRELIMINARY EXAMINATION REPORT

International application No. PCT/IB 03/04649

I. Basis of the report

1. With regard to the **elements** of the international application *(Replacement sheets which have been furnished to the receiving Office in response to an invitation under Article 14 are referred to in this report as "originally filed" and are not annexed to this report since they do not contain amendments (Rules 70.16 and 70.17))*:

Description, Pages

1-4, 6-21, 23	as originally filed
5, 22	filed with telefax on 08.10.2004

Claims, Numbers

1-23	as originally filed

Drawings, Sheets

1/3-3/3	as originally filed

2. With regard to the **language**, all the elements marked above were available or furnished to this Authority in the language in which the international application was filed, unless otherwise indicated under this item.

   These elements were available or furnished to this Authority in the following language: , which is:

   ☐ the language of a translation furnished for the purposes of the international search (under Rule 23.1(b)).

   ☐ the language of publication of the international application (under Rule 48.3(b)).

   ☐ the language of a translation furnished for the purposes of international preliminary examination (under Rule 55.2 and/or 55.3).

3. With regard to any **nucleotide and/or amino acid sequence** disclosed in the international application, the international preliminary examination was carried out on the basis of the sequence listing:

   ☐ contained in the international application in written form.

   ☐ filed together with the international application in computer readable form.

   ☐ furnished subsequently to this Authority in written form.

   ☐ furnished subsequently to this Authority in computer readable form.

   ☐ The statement that the subsequently furnished written sequence listing does not go beyond the disclosure in the international application as filed has been furnished.

   ☐ The statement that the information recorded in computer readable form is identical to the written sequence listing has been furnished.

4. The amendments have resulted in the cancellation of:

   ☐ the description, pages:

   ☐ the claims, Nos.:

   ☐ the drawings, sheets:

5. ☐ This report has been established as if (some of) the amendments had not been made, since they have been considered to go beyond the disclosure as filed (Rule 70.2(c)).

   (Any replacement sheet containing such amendments must be referred to under item 1 and annexed to this report.)

6. Additional observations, if necessary:

V. Reasoned statement under Article 35(2) with regard to novelty, inventive step or industrial applicability; citations and explanations supporting such statement

1. Statement

Novelty (N)	Yes:	Claims	1-23
	No:	Claims	
Inventive step (IS)	Yes:	Claims	1-23
	No:	Claims	
Industrial applicability (IA)	Yes:	Claims	1-23
	No:	Claims	

2. Citations and explanations

see separate sheet

AS TO BOX V:

1. The following document is cited:

   D1: DATABASE WPI Derwent Publications Ltd., London, GB; AN 1978-11823a XP002273274 CHERNOV R. V.: "electrolytic silicon-aluminium alloy production" & SU 554 318 A (AS UKR. INORGAN. CHEM.) 20 May 1977 (1977-05-20)

2. Document D1 discloses a fluoride containing molten electrolyte exhibiting a composition with alumina, aluminium fluoride, sodium fluoride and potassium as necessary components, the disclosed ranges of which comprise values that fall under the scope of present claim 1.

3. Although the electrolyte according to D1 requires e.g. 2.3 wt% SiO_2 for the formation of an Al-Si alloy, this component is not excluded by the definition given in claim 1. With regard to this claim 0-5% of one or more further constituents can be present.

4. Contrary to the disclosure of D1, which deals with the use of graphite anodes, claim 1, however, requires a metal-based anode. This establishes novelty over this prior art, so that the requirements of Art.33(2) PCT are met.

5. The problems to be solved with the present invention concern the provision of a cell with anodes that remain insoluble at the conditions applied during the production of aluminium and which can be operated without passivation or excessive contamination of the product. This requires, among others, a suitable adjustment of the composition of the electrolyte, which has moreover to remain crustless and ledgeless.

6. Although the ranges of the components disclosed in D1 overlap to a small extent with the ranges defined in claim 1, no hint can be derived from a document that suggests the use of graphite anodes, such as D1, to select conditions that prevent passivation or dissolution of metallic nickel, iron or cobalt.

7. Claim 1 with dependent claims 2-22 and method claim 23 are thus regarded as exhibiting an inventive step, required under Art.33(3) PCT.

Without being bound to any theory, it is believed that combining a high concentration of dissolved alumina in the electrolyte and a limited concentration of aluminium fluoride leads predominantly to the formation of (basic) fluorine-poor aluminium oxyfluoride ions ($[Al_2O_2F_4]^{2-}$) instead of (acid) fluorine-rich aluminium oxyfluoride ions ($[Al_2OF_6]^{2-}$) near the anode. As opposed to acid fluorine-rich aluminium oxyfluoride ions, basic fluorine-poor aluminium oxyfluoride ions do not significantly passivate the anode's nickel and cobalt, or dissolve the anode's iron. In particular, basic fluorine-poor aluminium oxyfluoride ions do not significantly passivate metallic nickel and cobalt, or dissolve iron oxides. The weight ratio of dissolved alumina/aluminium fluoride in the electrolyte should be above 1/7, and often above 1/6.5 or even above 1/6, to obtain a favourable ratio of the fluorine-poor aluminium oxyfluoride ions and the fluorine-rich aluminium oxyfluoride ions.

It follows that the use of the above described electrolyte with metal-based anodes containing at least one of nickel, cobalt and iron inhibits passivation and corrosion thereof.

In order to maintain the alumina concentration above the given threshold during normal electrolysis, the cell is preferably fitted with means to monitor and adjust the electrolyte's alumina content.

The abovementioned one or more further constituents of the electrolyte may comprise at least one fluoride selected from magnesium fluoride, lithium fluoride, cesium fluoride, rubidium fluoride, strontium fluoride, barium fluoride and cerium fluoride.

Advantageously, the cell is sufficiently insulated to be operated with a substantially crustless and/or ledgeless electrolyte. Suitable cell insulation is disclosed in US Patent 6,402,928 (de Nora/Sekhar), WO02/070784 and US Publication 2003/0102228 (both de Nora/Berclaz).

The cell can have a cathode that has an aluminium-wettable surface, in particular a drained horizontal or inclined surface. Suitable cathode designs are for example disclosed in US Patents 5,683,559, 5,888,360,

maintained around 8 weight% by periodically feeding fresh alumina into the cell.

After 50 hours electrolysis was interrupted and the anode extracted. Upon cooling the anode was examined externally and in cross-section.

The anode's outer dimensions as well as the anode's coating had remained substantially unchanged. However, TiO_2 had selectively been dissolved in the electrolyte from the coating. The anode's structure underneath the coating was similar to the structure observed in Examples 1 to 4.

Samples of the used electrolyte and the product aluminium were also analysed. It was found that the electrolyte contained less that 70 ppm nickel and the produced aluminium contained less than 300 ppm nickel which is significantly lower than with an uncoated anode that can cause a typical nickel contamination of 1000 ppm in the product aluminium.

Example 7

Example 6 can be repeated using different combinations of electrolyte compositions (A1-I1) selected from Table 1, anode alloy compositions (A2-K2) selected from Table 2 and coating compositions (A3-L3) selected from Table 3.

Further details on the application of such anode coatings and suitable compositions are disclosed in WO03/087435, WO2004/018731 and WO2004/024994 (all Nguyen/de Nora).

In summary, as can be seen by comparing Example 1-5 to the Comparative Example, using the potassium-fluoride electrolyte of the invention containing about 8 weight% dissolved alumina instead of a potassium-fluoride free electrolyte containing only 4 weight% dissolved alumina, inhibits fluorination and passivation of the nickel and/or cobalt of the anode and reduces wear (oxidation and dissolution of the anode's iron).